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(54) Title: A PELTIER DEVICE

(57) Abstract

A Peltier heat pump or refrigerator formed by a Peltier couple or array of Peltier couples which consist of a thermoelectrically active material with a high thermoelectric individual figure of merit in electrical contact with a high purity, high Debye temperature metal, preferably copper, aluminium or beryllium, to be operated at temperatures around and below 100 K.

A PELTIER DEVICE

Field of the Invention

The invention comprises a Peltier heat pump as may be used for the cooling and temperature control of electronic components for example.

Background

Peltier heat pumps or refrigerators can be used for the cooling and temperature control of electronic components such as infrared detectors, laser diodes and silicon-chip circuits. These devices typically comprise pairs of thermoelectric semiconductors formed into the branches of two or more junctions. When a current flows through such a junction or Peltier couple, heat flows into or out of the junction depending on the direction of the current. When two such junctions are connected in series, with opposite polarity, heat is transferred away from one junction and discharged at the other junction. The junction to which the heat is transferred is thermally connected to a heat sink and the other junction, referred to as the cold junction, will maintain a temperature below that of the heat sink when an appropriate current is applied.

The rate of transfer of heat from the cold junction to the heat sink is determined by a balance between the Peltier cooling, which is proportional to the current through the junctions and the Peltier coefficients of the two materials, the Joule heating which degrades the performance and is quadratic in

current, and the thermally conducted heat from the heat sink to the cold junction which is proportional to the temperature difference between the heat sink and the cold junction.

The optimum figure of merit, Z, for a Peltier couple built from two materials n and p, each forming one leg of the device, with thermopowers S_n and S_p, electrical resistivities r_n and r_p and thermal conductivities k_n and k_p is defined by the equation

$$Z = (S_n - S_p)^2/([r_nk_n]^{1/2} + [r_pk_p]^{1/2})^2$$

The maximum possible temperature difference, DT_{max}, between the heat sink and cold junction, resulting from the Peltier effect, is a function of the figure of merit

$$DT_{max} = ZT_c^2/2$$

where T_c is the temperature of the cold junction. A Peltier refrigerator thus normally requires materials which combine the properties of large thermopowers, small electrical resistivities and small thermal conductivities. This is usually achieved by choosing materials with the largest practical individual figures of merit

$$z = S^2/rk$$

where S, r and k are the thermopower, electrical resistivity and electrical conductivity of the material. Semiconductors fill this role in applications at and around room temperature.

For operation in the temperature range 250 to 450K semiconducting alloys such as doped bismuth telluride materials appear to be among the best materials for both the p-type and n-type elements, with individual figures of merit of around 3×10^{-2} K^{-1}. In this temperature range metals are unsuitable as a replacement material for either branch in a Peltier heat pump. Although they may have a small electrical resistivity they also have small thermopowers compared with semiconductors and high thermal conductivity. At these temperatures metals generally satisfy the Wiedemann-Franz law which states that the ratio of the thermal conductivity to the electrical conductivity is directly proportional to the temperature

$$rk \geq (pk_B)^2 T/3e^2$$

Thus the increased thermal leakage of heat from the heat sink to the cold junction outweighs the benefit of reduced Joule heating.

At lower temperatures, in the neighbourhood of liquid nitrogen (77K), the best known materials for the n-type branch of the couple consist of bismuth-rich alloys of bismuth and antimony. The figure of merit of this material can be optimized by the application of a magnetic field. For example, $Bi_{85}Sb_{15}$ at 80K has a z of 6×10^{-3} K^{-1} in a magnetic field of 0.0 Tesla and a z of 11×10^{-3} K^{-1} in a field of 0.13 Tesla. However the best p-type semiconductors, bismuth tellurium alloys, have high electrical resistance which results in a z of less than 2×10^{-3} K^{-1} at the same temperature and severely limits the performance of low temperature Peltier heat pumps.

Summary of the Invention

In broad terms the present invention comprises a Peltier heat pump comprising a Peltier junction or couple or array of junctions or couples formed between a thermoelectrically active material and a metallic material with a high Debye temperature to form a Peltier couple or array of Peltier couples.

Preferably the Debye temperature of the pure metal is in excess of 340K, further preferably above 500K and most preferably in excess of 1000K.

Preferably the thermoelectrically active material is a semiconducting material and most preferably an n-type semiconductor, or alternatively a semi-metallic material having a high individual figure of merit, which is preferably chosen to optimise the figure of merit of the Peltier couple(s) at temperatures around and below 100K.

Preferably the figure of merit at the temperature of operation is at least $5x10^{-3}K^{-1}$, further preferably above $6.5x10^{-3}K^{-1}$ and most preferably in excess of $10x10^{-3}K^{-3}$.

Certain metals in very pure form exhibit the property that, at temperatures intermediate to room temperature and absolute zero, rk may fall significantly below the classical Wiedemann-Franz value. For example, in Cu at 80K, rk can fall

to a factor of 2 below the classical limit while in Be it may fall below the classical limit even further.

The thermopower of such a metal in the couple is negligible relative to that of the thermoelectrically active branch and hence it contributes little to the Peltier heat pumping within the couple. However because the product of the metal's thermal conductivity and electrical resistivity is also small it also makes only a small contribution to the Joule heating and heat leakage which limit the couple's performance and the maximum temperature drop obtainable.

Thus a couple formed from for example an n-type semiconductor with a high individual figure of merit and a pure metal can have a larger figure of merit than that obtainable using the same n-type semiconductor in association with the best available p-type material.

Metals that may be used in the junction include Be; Cr, Ru, Os; Rh, Fe, Mo, Ni, Co, Re, Al, Ti, Mn; and Mo, U, V, Sc, and Cu. However, any pure metal having an acceptable Debye temperature may be used.

Preferably the purity of the metal is as high as possible and in excess of 99.5% pure, further preferably in excess of 99.9% pure and most preferably in excess of 99.99% pure. The purity should be sufficiently high that the electron

mean free path is limited by the lattice vibrations rather than by impurities or defects, down to the temperature at which the device is operated.

Preferably the metal arm is annealed in vacuum to reduce the density of grain boundaries, preferably to a level that the dimensions of the crystalline grains are greater than a few hundred nanometres. Preferably a pure aluminium arm should be annealed at a temperature above 200°C, a pure copper arm should be annealed at a temperature above 400°C and a pure Beryllium arm should be annealed at a temperature above 500°C.

A magnetic field of up to 0.2Tesla may be applied to the junction while in operation to optimize the individual figure of merit of the thermoelectrically active material. Fields of this magnitude should have a negligible effect on the thermal and electrical conductivity of the metallic element.

A preferred thermoelectrically active material that can be used in the junction is $Bi_{1-x}Sb_x$ where x is in the range 0.15±0.05. Any other thermoelectrically active n-type material with a similar or higher figure of merit than bismuth antimonide may also be used in the active leg in the junction. Alternatively a p-type material with a figure of merit comparable to or higher than existing n-type materials could be used in the active leg of the junction.

Description of the Drawings

The invention will be further described with reference to the accompanying drawings by way of example and without intending to be limiting, wherein:

Figs 1a and 1b are schematic diagrams of single Peltier couples of the invention,

Figs 2a and 2b are schematic diagrams of arrays of Peltier couples of the invention, and

Figs 3a and 3b are schematic diagrams of cascaded Peltier couples of the invention.

Description of Preferred Forms of the Invention

With reference to Figs 1a and 1b the semiconducting leg of the couple (1) preferably comprises an alloy of bismuth and antimony with composition $Bi_{1-x}Sb_x$ where x is preferably in the range 0.15±0.05. The metallic leg of the couple (2) preferably comprises a high purity, high Debye temperature metal, preferably aluminium, beryllium or copper.

The connection between the semiconducting and metallic branches of the couple may be formed directly by a low electrical resistance bond (3) between the two branches as shown in Fig. 1a, or by an intermediate material with high thermal conductivity and high electrical conductivity (4), for example aluminium or

copper, which is itself bonded to both the semiconducting leg and the metallic leg, as shown in Fig. 1b.

The hot junction ends of each leg should be similarly bonded to materials with high thermal conductivity and high electrical conductivity (5,6), for example aluminium or copper or other metals with high thermal conductivity, to form the heat-sink for the couple. The heat sink may be cooled to the operating temperature by a bath of liquid nitrogen or other cryogen, or a closed cycle refrigerator, or by the cold junction of a further Peltier cooler. Current leads (7,8) are electrically connected to the heat-sink elements (5,6) and a current supply (9). The region of the cold junction is shown by the label (cj) and the heat sink by the label (sk).

The current required to operate a cooler depends on the dimensions of the couple and it's heat pumping capacity but typically Peltier couples are high current, low voltage, devices. The required operating temperature of the cold junction would be maintained preferably by controlling the current supplied to the cooler.

The Peltier heat pump may consist of a single couple as shown in Fig. 1. or a linear or x-y array of such couples as shown in Figs 2a and 2b respectively.

In Fig. 2, m is a metallic leg, n is a semiconducting leg, c indicates electrical connecting materials, i indicates electrical insulators, cj indicates the cold junction, sk indicates the heat sink and + and - denote the current leads.

The cold junction at the top of the couple provides the zone which is cooled when an electric current is passed through the device. When an array of couples is assembled as illustrated schematically in Fig. 2 these cooled zones may be linked by a body i, preferably a sheet or plate, which is a good electrical insulator and a good thermal conductor. This body may then act as a heat sink for whatever devices or components may be connected to it.

This form of construction is illustrative and not limiting in generality. Other forms are known in the art of Peltier heat pump construction and may be preferable in some applications. Monolithic Peltier couples may be constructed in which the legs are separated, except at the cold junction, by an insulating layer. The legs of the couple and any such insulating layers may be in the form of thick or thin films.

Figs 3a and 3b show two ways in which a sequence of Peltier couple arrays may be cascaded in two stages to increase the temperature difference between the heat sink and cold junction. m is a metallic leg, n is a semiconducting leg, c indicates electrical connecting materials, i indicates electrical

insulators, cj indicates the cold junction, sk indicates the heat sink and + and - denote the current leads. This form of construction is illustrative only and not limiting in general. Arrays of couples may be cascaded through several stages to achieve even greater temperature drops. In a cascaded array different pure metals may be used as the metallic branch of the Peltier couple in different levels of the cascade in order to optimize performance.

Although the metals used in the metallic legs of the Peltier couples do have a measurable thermopower it is negligible relative to that of the semiconducting material. Therefore the Peltier couples of the invention can be compared to the prototype couples comprising a thermoelectrically active leg joined to a thermoelectrically passive leg as described in papers written by the inventors M G Fee, Applied Physics Lett. 62, 1161 (1993), and H J Trodahl and M G Fee, Proc. of the 6th Int. Symposium on Superconductors (ISS93), Hiroshima, October 26-29, 1993 (Springer-Verlag, Tokyo) to be published.

A prototype device was built consisting a single couple between an oriented crystal of $Bi_{79}Sb_{21}$ and 5-9 pure copper wire. The $Bi_{79}Sb_{21}$ crystal had a length of 1.1cm and a cross-sectional area of $0.06cm^2$, while the wire (which had been annealed in vacuum at a temperature of 500°C) was 1mm in diameter and 43cm long in order to maximise the figure of merit for the couple. A temperature drop of 4.2 degrees below that of liquid nitrogen

was obtained at a current of 2.5A in zero field and a drop of 4.9 degrees in a field of 0.07T.

We have calculated that a Peltier couple formed between $Bi_{0.85}Sb_{0.15}$ and high purity aluminium would produce a temperature drop of 7.5 degrees when operated with the heat sink held at 77K, increasing to 14 degrees in a magnetic field of 0.12T. Temperature drops of twice these figures are in principle possible with a two-stage heat pump, although the enhanced temperature drop in this configuration deteriorates as the efficiency of the device (Q_{cool}/Q_{hot}) rises to a few percent.

The forgoing describes the invention including preferred forms thereof. Alterations and modifications as will be obvious to those skilled in the art are intended to be incorporated within the scope hereof as defined in the following claims.

CLAIMS

1. A Peltier heat pump, comprising a junction or array of junctions between a thermoelectrically active material and a metallic material with a high Debye temperature to form a Peltier couple or array of Peltier couples.

2. A Peltier heat pump according to claim 1, wherein the thermoelectrically active material is a semiconductor.

3. A Peltier heat pump according to claim 2, wherein the thermoelectrically active material is an n-type semiconductor.

4. A Peltier heat pump comprising a junction or array of junctions between an n-type semiconducting material with a high individual figure of merit at the temperature of operation and a pure metal having a high Debye temperature.

5. A Peltier heat pump according to any of claims 2 to 4, wherein the semiconducting material is chosen to optimise the figure of merit of the Peltier couple at a temperature below 100K.

6. A Peltier heat pump according to either one of claims 1 and 4, wherein the semiconducting material is n-type $Bi_{1-x}Sb_x$ with $x=0.15\pm0.05$.

7. A Peltier heat pump according to any one of claims 1 to 3, and 5 and 6 when dependent on 1 to 3, wherein the metallic material is a high purity metal.

8. A Peltier heat pump according to any one of claims 1 to 7, wherein the metallic material has a Debye temperature in excess of 340K.

9. A Peltier heat pump according to any one of claims 1 to 7, wherein the metallic material has a Debye temperature in excess of 500K.

10. A Peltier heat pump according to any one of claims 1 to 9, wherein the metallic material is a metal of purity in excess of 99.5%.

11. A Peltier heat pump according to any one of claims 1 to 9, wherein the metallic material is a metal of purity in excess of 99.9%.

12. A Peltier heat pump according to any one of claims 1 to 11, wherein the metallic material is selected from the group Cr, Ru, Os; Rh, Fe, Mo, Ni, Co, Re, Ti, Mn, Mo, U, V and Sc.

13. A Peltier heat pump according to any one of claims 1 to 11, wherein the metallic material is selected from the group Al, Be, Cu.

14. A Peltier heat pump according to any one of claims 2 to 13, wherein the metallic material of the Peltier couple is a single crystal.

15. A Peltier heat pump according to any one of claims 2 to 14, wherein the metallic material of the Peltier couple has been annealed to maximise the figure of merit of the couple.

16. A Peltier heat pump according to any one of claims 2 to 15, wherein the semiconducting material of the Peltier couple is a single crystal.

17. A Peltier heat pump according to any one of claims 2 to 16, wherein the semiconducting material has been crystallographically oriented to maximize its individual figure of merit.

18. A Peltier heat pump according to any one of claims 2 to 17, wherein the junction figure of merit is greater than $3 \times 10^{-3}\ K^{-1}$.

19. A Peltier heat pump according to any one of claims 2 to 18, wherein a magnetic field is applied either to the semiconducting material of the Peltier couple or to the whole couple, either by permanent magnets or electromagnets.

20. A Peltier cooler comprising a multiple number of individual Peltier couples according to any one of claims 1 to 19, combined thermally in parallel, in a one or two dimensional array, such that the cold junctions act together to provide greater cooling.

21. A Peltier cooler comprising a multiple number of Peltier cooling stages each comprising an individual Peltier couple or a multiple number of Peltier couples according to any one of claims 1 to 19 combined thermally in parallel, in a one or two dimensional array, cascaded such that the heat sink or sinks of one cooling stage is/are cooled by the cold junction(s) of another cooling stage.

22. A method of cooling utilizing a Peltier heat pump or Peltier cooler according to any one ,of the preceding claims, wherein the heat sink is cooled to and operated at a temperature around or below 100K.

23. A Peltier heat pump substantially as herein described with reference to any one or more of the accompanying drawings.

Fig 1a

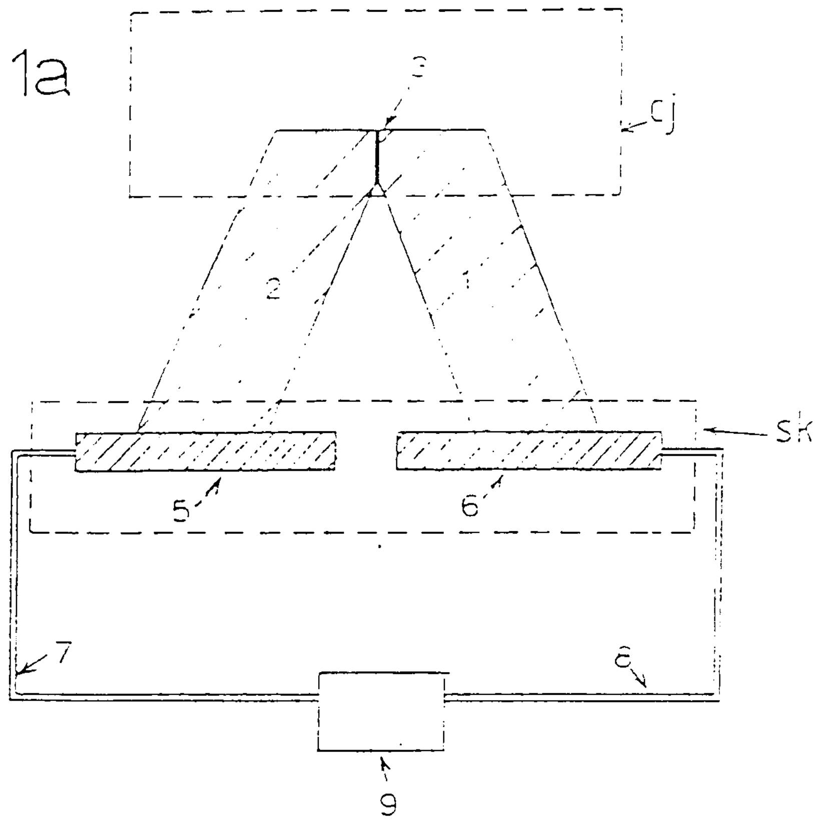


Fig 1b

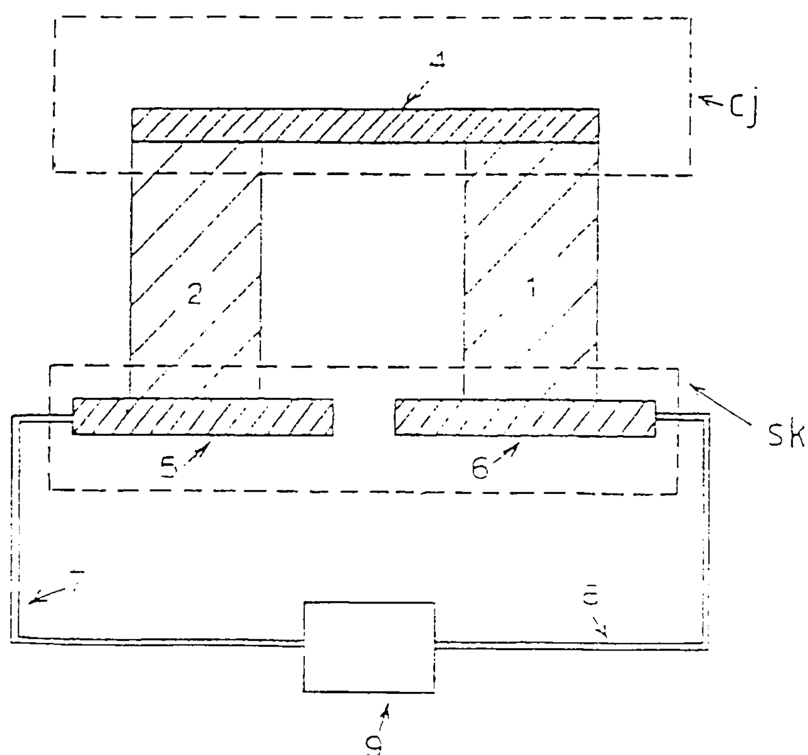


Fig 2a

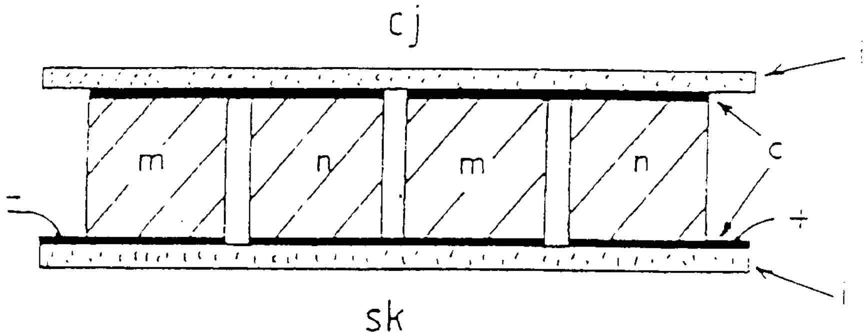


Fig 2b

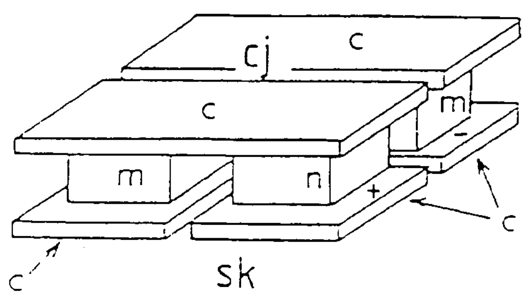


Fig 3a

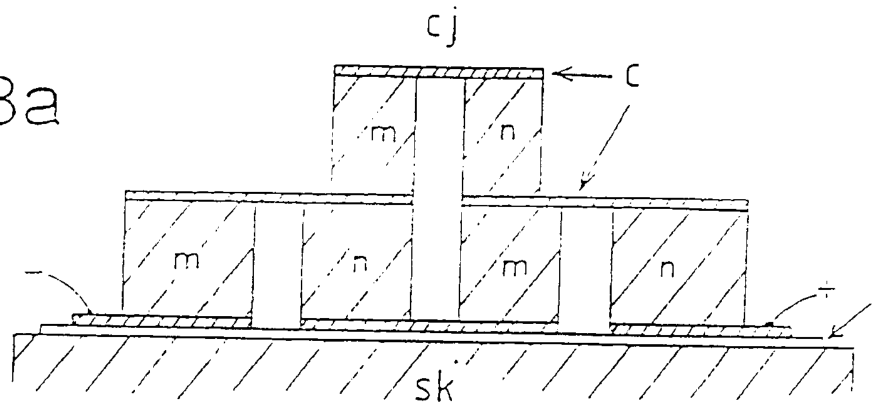
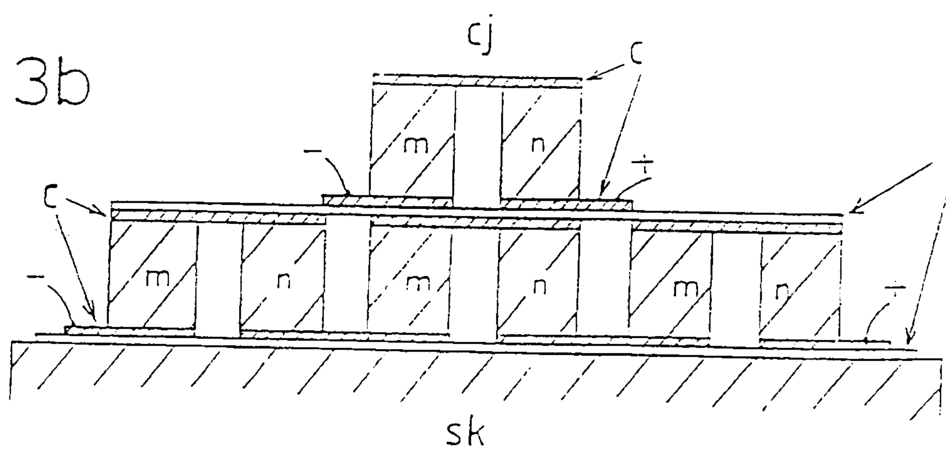


Fig 3b



INTERNATIONAL SEARCH REPORT

International application No.
PCT/NZ 94/00045

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.[5] F25B 21/02, H01L 35/28, 23/38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC : F25B 21/02, H01L 35/28, 23/38

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU : IPC marks as above

Electronic data base consulted during the international search (name of data base, and where practicable, search terms used)
DERWENT : IPC marks as above and Peltier:

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	US,A, 3090207 (SMITH et al) 21 May 1963 (21.05.63) Column 3 lines 18-29	1-4,13
P,X	Patent Abstracts of Japan, M-1502, page 74, & JP,A, 5-172424 (MATSUSHITA ELECTRIC IND. CO. LTD) 9 July 1993 (09.07.93) Abstract	1,2,13
X	EP,A2, 275829 (AGROGEN-STIFTUNG) 27 July 1988 (27.07.88) column 3 lines 27-46, figure 2, Example	1-4,13
A	AU,B, 27976/89 (627705) (CHEMONORM AG) 1 August 1989 (01.08.89) entire document	1-23

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 August 1994 (22.08.94)	26 August 1994 (26.08.94)
Name and mailing address of the ISA/AU AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No. 06 2853929	Authorized officer R. HOWE Telephone No. (06) 2832159

International application No.
PCT/NZ 94/00045

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
EP	275829	AU	10360/88	CH	672834	JP	63273466
		US	4799358	BR	8806996		
AU	27976/89	BR	8807399	CH	675154	DK	4370/89
		EP	350502	FI	894038	NO	893534
		WO	8906335				

END OF ANNEX